

Processes of ammonia adsorption in gallium zeolites as studied by microcalorimetry

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Abstract

In adsorption calorimetric studies, it is necessary to analyse the obtained calorimetric and volumetric data in relation to coverage or number of sites. For this purpose, procedures have been developed to relate quantitative measurements of heat liberation to the different processes which are taking place as the amount of adsorbed ammonia increases, due to reversible and irreversible adsorption. In order to describe the relative contributions of these two phenomena (physical and chemical adsorption) to volumetric isotherms as well as to calorimetric thermograms, they have been modeled and chemisorption was separated from physisorption. Calorimetric and volumetric measurements performed on H-[Ga]-BEA and H-[Ga]-MFI zeolites have provided experimental data to validate the theoretical models. The acidity of the gallium samples has been compared with that of the corresponding aluminum samples. © 1998 Elsevier Science B.V.

Keywords: Ammonia adsorption; Gallium zeolites; Microcalorimetry

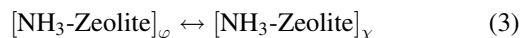
1. Introduction

Since the catalytic properties of zeolites are determined mainly by their acidity, it is very important to develop correct methods for studying their acid centers. Ammonia is widely used to determine the number and strength of acid sites in zeolitic systems. The calorimetric measurement of the heat evolved during the adsorption of bases seems to be the most direct and accurate method for the determination of the acid strength distribution, i.e. for the determination of the strength of acid sites as a function of coverage [1]. However, in practice, very few data are available on the mechanisms of NH₃ adsorption at low and high coverages on centers of different types.

In adsorption calorimetric studies, it is necessary to analyse the obtained calorimetric and volumetric data in relation with coverage or number of sites. For this purpose, procedures have been developed to relate the quantitative measurements of heat liberation to the different processes which are taking place as the amount of adsorbed ammonia increases.

The adsorption processes with weak interaction energies, such as physisorption, should be influenced by multilayer formation of molecules and by mutual interactions between adsorbed molecules. Meanwhile, the adsorption processes with strong interaction energies, such as chemisorption, should be influenced mostly by the interaction between the ammonia dipole and the electric field from the Brønsted- or Lewis-acid sites. Indeed, the following reactions represent the mechanism of interaction between the gaseous probe molecule and the surface:

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Equilibrium (1) describes the physical adsorption process, and $[\text{NH}_3\text{-Zeolite}]_{\varphi}$ implies that NH_3 is adsorbed physically. Equilibrium (2) describes the chemical adsorption process, and $[\text{NH}_3\text{-Zeolite}]_{\chi}$ implies that NH_3 is adsorbed chemically. Equilibrium (3) describes the transformation of physically adsorbed NH_3 to a chemisorbed species (occupancy of more energetically active centers).

In order to describe the relative contributions of these two phenomena (physical and chemical adsorption) in volumetric isotherms as well as in the calorimetric thermograms, we have modeled them so as to separate the chemisorption from the reversible adsorption.

Since recent studies have shown that isomorphous replacement of aluminum by gallium in the framework structure of zeolites offers new opportunities for modified catalytic activity [2,3], it was of particular interest to study gallium zeolites (H-[Ga]-BEA and H-[Ga]-MFI) for the experimental validation of the models. Insertion of T atoms such as Ga with lower charge density than Al in the lattice framework could affect acid sites strength and distribution and generate more coke-selective materials.

2. Experimental

The experiments were performed on an H-[Ga]-BEA (Si/Ga=40) and an H-[Ga]-MFI (Si/Ga=52). Ga-MFI and Ga-BEA crystals were synthesized from galliosilicate hydrogels with molar composition $\text{Ga}_2\text{O}_3 : 100\text{SiO}_2 : 5\text{Na}_2\text{O} : 5(\text{TPA})_2\text{O} : 1500\text{H}_2\text{O}$ and $\text{Ga}_2\text{O}_3 : 100\text{SiO}_2 : 12(\text{TEA})_2\text{O} : 1285\text{H}_2\text{O}$, respectively, where TPA and TEA are tetrapropyl and tetraethyl ammonium cations. Crystallization was conducted in Teflon-lined Berghoff autoclaves with stirring. Following oxidative decomposition in air, the Ga-MFI crystals were exchanged with a 1 M NH_4NO_3 solution at 333 K for 2 h. The $\text{NH}_4\text{-[Ga]-MFI}$ was then heated to 813 K during 4 h to obtain its H-form. The H-[Ga]-MFI crystals thus obtained had a BET surface area of $385 \text{ m}^2/\text{g}$, a pore volume of $0.26 \text{ cm}^3/\text{g}$ and

contained 2.07 wt% Ga to yield a Si/Ga molar ratio of 52. The H-[Ga]-BEA crystals obtained similarly had a surface area of $534 \text{ m}^2/\text{g}$ and contained 2.74 wt% Ga to yield a Si/Ga molar ratio of 40. The ^{71}Ga MASNMR spectra contain only one single resonance, consistent with framework Ga(IV). However, second-order quadrupolar broadening effects could have prevented the observation of extraframework Ga(VI) species [4].

Differential heats of NH_3 adsorption were measured using a Tian–Calvet type microcalorimeter connected with a volumetric vacuum adsorption line for the determination of the adsorbed amounts. The details of the method are well known and described elsewhere [5–8]. The samples were pretreated overnight under vacuum at 773 K and the adsorption was carried out at 423 K. After adsorption was completed and an equilibrium pressure of ca. 0.6 torr was reached, the samples were outgassed by pumping at the same temperature and then a secondary adsorption was performed under the same experimental conditions. During the primary adsorption, both reversible adsorption (called here physisorption) and irreversible adsorption (called here chemisorption) are expected, while the secondary adsorption corresponds only to reversible adsorption (physisorption). The calorimetric and volumetric measurements have provided experimental data to validate the theoretical models.

3. Results and discussion

3.1. Experimental data

The variations of the differential heat of adsorption of ammonia with coverage on H-[Ga]-BEA and H-[Ga]-MFI are given in Fig. 1. The heats of adsorption decrease with coverage for all samples, i.e. the acid strength distributions are heterogeneous, but present a small plateau, ca. 115 kJ/mol for H-[Ga]-BEA and 150 kJ/mol for H-[Ga]-MFI. The corresponding volumetric isotherms can be found in Figs. 2 and 3 (experimental curves).

A comparison between the two zeolites studied reveals that the site distribution is more heterogeneous for H-[Ga]-BEA, while H-[Ga]-MFI presents a clearly visible plateau near 150 kJ/mol and only very few stronger sites, H-[Ga]-BEA presents two distinct site populations, one with heats ca. 115 kJ/mol and a

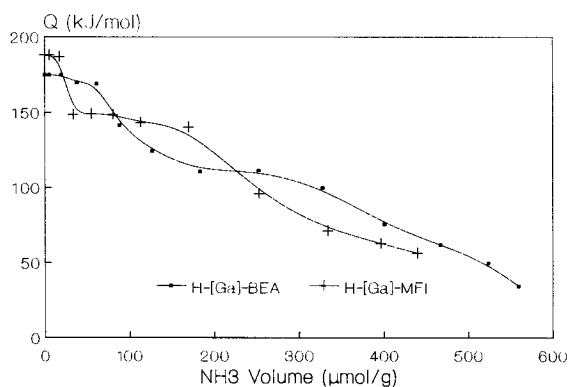


Fig. 1. Differential heat of ammonia adsorption at 423 K vs. coverage for H-[Ga]-BEA and H-[Ga]-MFI zeolites.

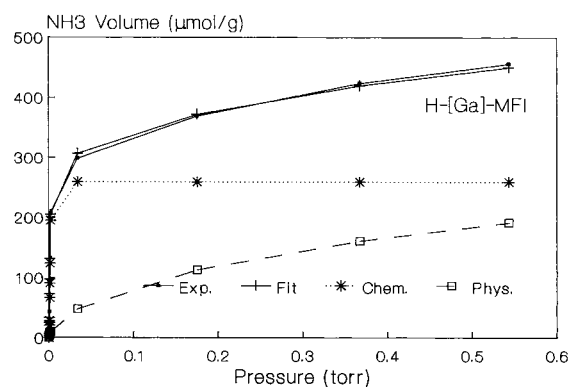


Fig. 3. Volumetric isotherm decomposition into physisorption and chemisorption parts for sample H-[Ga]-MFI at 423 K.

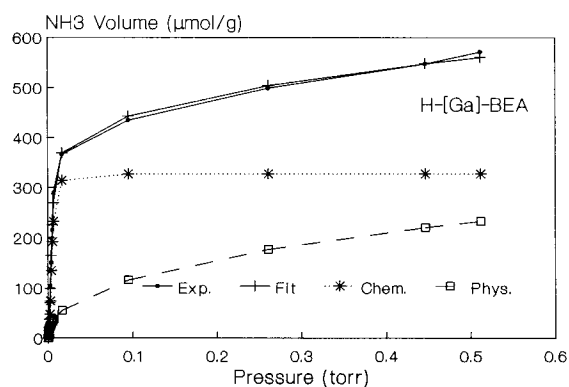


Fig. 2. Volumetric isotherm decomposition into physisorption and chemisorption parts for sample H-[Ga]-BEA at 423 K.

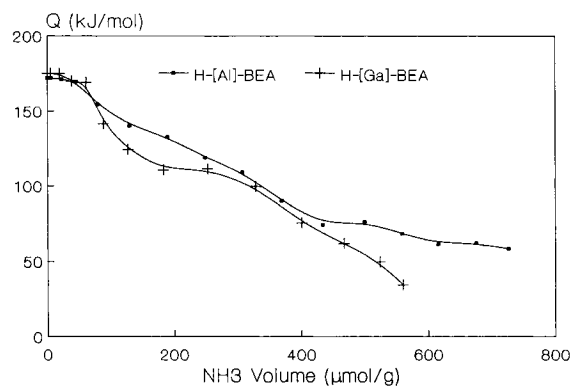


Fig. 4. Differential heat of ammonia adsorption at 423 K vs. coverage for H-[Al]-BEA and H-[Ga]-BEA zeolites.

smaller one ca. 170 kJ/mol. These two distinct site populations in H-[Ga]-BEA could be related to differences in ammonia diffusion rates as coverage varies.

Parrillo et al. [9] studied (at 480 K) an H-[Ga]-ZSM-5 sample containing 410 Ga μmol/g and a pore volume of 0.17 cm³/g. The differences between their sample and the sample studied (288 μmol/g Ga and pore volume of 0.26 cm³/g) and the different adsorption temperatures prevent any straightforward comparison between the two studies. Parrillo et al. report a fairly large population of sites (~350 μmol NH₃/g) with strength near 150 kJ/mol, while our sample contains a small population of very strong sites >150 kJ/mol which may be ascribed to the presence of some extraframework gallium. Furthermore, Fig. 1 displays an inflection point near 250 μmol/g for

H-[Ga]-MFI, which is consistent both, with the irreversibly adsorbed volume (259 μmol/g, see Table 1 below) and the gallium content as determined by chemical analysis.

The gallium samples were also compared with the corresponding aluminum forms H-[Al]-MFI and H-[Al]-BEA in Figs. 4 and 5. The H-[Al]-BEA sample presents an Si/Al ratio of 14.6 from chemical analysis and 11.2 from ²⁷Al NMR and displays a heterogeneous population of acid sites showing a differential heat curve continuously decreasing as a function of the ammonia coverage (Fig. 4). The two differential heat curves for H-[Al]-BEA and H-[Ga]-BEA show similar initial heat values ca. 170 kJ/mol, but they are otherwise very dissimilar. The Si/Al and Si/Ga ratios are not close enough for a very valuable comparison and the

Table 1

Zeolite	Si/Ga	Chemisorption			Physisorption		
		n_{χ}^0 / $\mu\text{mol/g}$	K_{χ} / torr^{-1}	α_{χ}	n_{φ}^0 / $\mu\text{mol/g}$	K_{φ} / torr^{-1}	α_{φ}
H-[Ga]-BEA	40	327	220	2.43	3334	5.29×10^{-3}	0.44
H-[Ga]-MFI	52	259	712	2.82	727	0.317	0.59

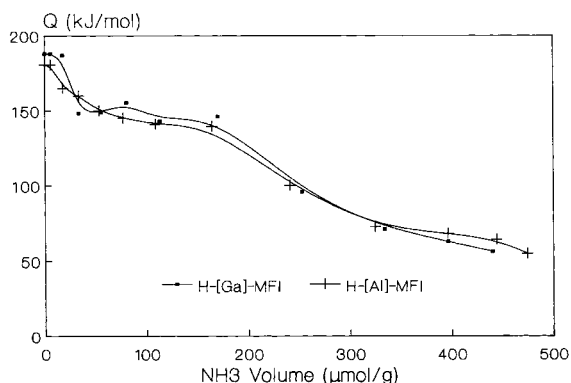


Fig. 5. Differential heat of ammonia adsorption at 423 K vs. coverage for H-[Al]-MFI and H-[Ga]-MFI zeolites.

irreversibly adsorbed volumes are ca. 408 $\mu\text{mol/g}$ for H-[Al]-BEA and only 327 $\mu\text{mol/g}$ for H-[Ga]-BEA. The H-[Al]-MFI sample presents a Si/Al ratio of 63 from chemical analysis and displays a curve of differential heat vs. the ammonia uptake (Fig. 5) very close to that of the gallium sample. The irreversibly adsorbed volume is 264 $\mu\text{mol/g}$ for H-[Al]-MFI compared to 259 $\mu\text{mol/g}$ for H-[Ga]-MFI. In that case, the comparison of the two curves is fully valid because the samples have similar Si/Ga and Si/Al ratios. It appears that the substitution of Al by Ga does not create a large number of strong sites.

3.2. Modeling of volumetric isotherms

The volumetric isotherms (number of adsorbed molecules n as a function of the pressure P) consist of two distinct parts. The nearly vertical part corresponds mostly to chemisorption, while the nearly horizontal part corresponds mostly to physisorption. Each one of the two processes was found to follow the model of Sips (modified Langmuir–Freundlich isotherm) [10–16]. Thus, the volumetric isotherm is

described by a sum of two Sips isotherms, one for chemisorption and one for physisorption. Sips isotherms are described by the following equation:

$$n = n^0 \frac{(KP)^\alpha}{1 + (KP)^\alpha}$$

where n^0 is a characteristic volume, K the equilibrium constant (homogeneous to the inverse of pressure P) and α a characteristic exponent.

Let n be the total adsorbed ammonia amount, n_{φ} the amount corresponding to physisorption, and n_{χ} the amount corresponding to chemisorption. These two amounts correspond to Sips isotherms with two different sets of parameters:

$$n_{\chi} = n_{\chi}^0 \frac{(K_{\chi}P)^{\alpha_{\chi}}}{1 + (K_{\chi}P)^{\alpha_{\chi}}} \quad \text{and} \quad n_{\varphi} = n_{\varphi}^0 \frac{(K_{\varphi}P)^{\alpha_{\varphi}}}{1 + (K_{\varphi}P)^{\alpha_{\varphi}}},$$

and $n = n_{\chi} + n_{\varphi}$. In order to obtain the decomposition $n = n_{\chi} + n_{\varphi}$ from the experimental data, it is necessary to first model the secondary volumetric isotherm obtained during the readsorption. This secondary isotherm describes solely the phenomenon of physisorption. Thus, we can first determine the Sips parameters for physisorption from the secondary isotherm, and then subtract the physisorption isotherm from the primary global isotherm in order to obtain solely the part corresponding to chemisorption, which then provides the Sips parameters for chemisorption.

All curve-fitting parameters were obtained by using a non-linear least-squares fitting model. However, great care should be taken when computing these Sips parameters, since they are very sensitive to the pressures measured at low coverages. Table 1 gives the volumetric isotherm decomposition parameters for the two zeolites studied.

Figs. 2 and 3 show the experimental volumetric isotherms and the theoretical fitted curves for physi-

sorption and chemisorption on H-[Ga]-BEA and H-[Ga]-MFI, respectively. These curves show that, at low pressures, chemisorption is very predominant, but that physisorption becomes the only detectable process as soon as the pressure reaches 0.03 torr. Moreover, chemisorption concerns only a limited number of sites, close to the parameter n_{χ}^0 , whereas reversible adsorption can potentially occur on a much larger number of sites.

3.3. Modeling of thermograms

The recorded thermal heat flow for each dose of gas, as a function of time, can also be decomposed into two parts, one corresponding to chemisorption and the other to physisorption. Each part was observed to fit with the model of an asymmetric double sigmoidal function:

$$D_{[D_{\max}, \alpha, \beta, \tau_1, \tau_2]}(t) = \frac{D_{\max} \exp(-\tau_2^{-1}(t - \alpha - \beta/2))}{[1 + \exp(-\tau_1^{-1}(t - \alpha + \beta/2))][1 + \exp(-\tau_2^{-1}(t - \alpha - \beta/2))]}$$

where $D(t)$ is the recorded signal, t the time, D_{\max} the maximum recorded signal, τ_1 the *time of rise* and τ_2 the *time of relaxation*, and α and β are homogeneous with respect to time.

Both parts D_{χ} and D_{φ} of the heat flow are described by this model, each part having its own set of parameters ($D_{\max}, \tau_1, \tau_2, \alpha, \beta$). As was done for isotherms, in order to obtain the decomposition $D = D_{\chi} + D_{\varphi}$ from the experimental data, it is necessary to first model the secondary thermograms obtained during the readsorption, which describe only the phenomenon of physisorption. Thus, we can first determine the parameters for physisorption from the readsorption thermograms. The parameters $\tau_{1\varphi}$ and $\tau_{2\varphi}$, which describe the intrinsic shape of the thermogram, were found to be nearly the same for all readsorption peaks: for both samples, we observed $\tau_{1\varphi} \approx 8$ and $\tau_{2\varphi} \approx 95$ s.

Thus, each primary thermogram was fitted with the sum of two asymmetric double sigmoidal functions, one with arbitrary parameters corresponding to chemisorption and the other with parameters $\tau_{1\varphi}$ and $\tau_{2\varphi}$, identical to those of readsorption thermograms corresponding to physisorption. If the parameters $\tau_{1\varphi}$ and $\tau_{2\varphi}$ computed from readsorption thermograms vary with coverage, the values that must be taken for the

decomposition of a given primary thermogram are those which correspond to the same pressure.

As an example, Fig. 6 shows the decomposition of a typical adsorption peak (H-[Ga]-BEA, coverage between 100 and 150 $\mu\text{mol/g}$) into chemisorption and physisorption parts.

Figs. 7 and 8 show, for the two samples, the time of chemisorption relaxation ($\tau_{2,\chi}$) obtained by fitting the experimental peaks, and the percentage of the peak area due to chemisorption computed by comparing the area of the fitted chemisorption peak with the total area of the experimental peak. In both cases the chemisorption percentage globally decreases with coverage, but remains very high (ca. 70–80%) during the peaks associated with strong adsorption. Then the chemisorption fraction drops drastically as the thermogram becomes identical to readsorption thermograms. The chemisorption time of relaxation ($\tau_{2,\chi}$)

was always greater than that associated with physisorption. This confirms that chemisorption is a slower process than physisorption. The estimated time of relaxation for chemisorption was observed to first increase at very low coverage, then go through a maximum, and finally gradually decrease to reach the physisorption value when the adsorption becomes less energetic.

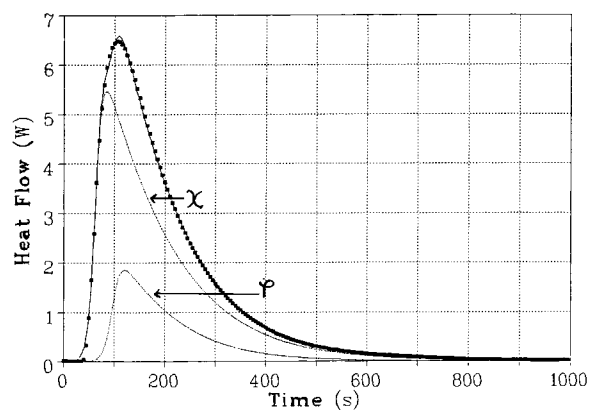


Fig. 6. Calorimetric thermogram decomposition for a typical adsorption peak (H-[Ga]-BEA).

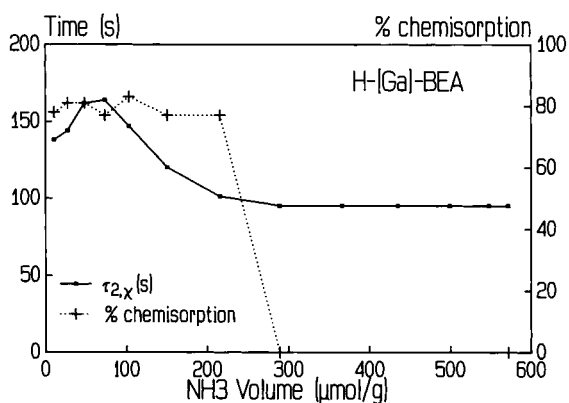


Fig. 7. Chemisorption time of relaxation ($\tau_{2,x}$) and percentage of the peak area due to chemisorption vs. coverage for sample H-[Ga]-BEA.

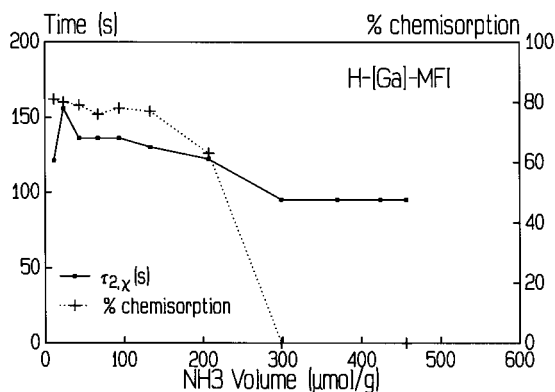


Fig. 8. Chemisorption time of relaxation ($\tau_{2,x}$) and percentage of the peak area due to chemisorption vs. coverage for sample H-[Ga]-MFI.

4. Conclusion

This study has shown that it is possible to model separately the reversible and irreversible adsorption processes, as studied by microcalorimetry, in such a

way as to obtain results that are coherent with experimental data. Moreover, equations allowing access to quantities such as the entropies of adsorption and the differential heats, independently for each process, could be derived from the models. However, such a program requires a thorough checking of the correspondence between the various adsorption sites and the various subprocesses identified by the model. Thus, improved models may be necessary before a complete description of the competition between adsorption processes can be obtained.

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